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Advances in producing cost-effective direct borohydride fuel cells and road to its commercialization

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Abstract

A direct borohydride fuel cell (DBFC) converts chemical energy stored in borohydride ion (BH_4^-) and an oxidant directly into electricity by redox processes. Usually, a DBFC employs an alkaline solution of sodium borohydride ($NaBH_4$) as fuel and oxygen or hydrogen peroxide as oxidant. Some of the attractive features in DBFC include high open circuit potential, ease of electro-oxidation of BH_4^- on non-precious metals, such as nickel, low operational temperature and high power density. The DBFC is a promising power system for portable applications. The biggest barriers to its commercialization are its high cost and long-term stability. This paper discusses some of the recent advances made in reducing the cost of DBFC. The technology is reaching a point where it could soon be commercialized. The effect of the reduced cost on its commercialization is discussed in this paper.

Keywords: Direct borohydride fuel cell; catalyst material; catalyst binder; chitosan membrane; PVA membrane;

1. Introduction

A fuel cell is an electrochemical energy device that converts chemical energy of the fuel into electrical energy. Unlike a battery, which stores a finite amount of energy, a fuel cell continues to produce energy as long as the oxidant and fuel are fed into it. A fuel cell is inherently energy efficient, environmentally friendly and silent. The polymer electrolyte fuel cell (PEFC) employs polymer membrane as the electrolyte. Compared to other types of fuel cells, it is capable of achieving reasonably high power performance at relatively low working temperatures ($\leq 100\ ^oC$) and thus is considered a promising power supply for transport, stationary, and also portable applications. The direct borohydride fuel cell (DBFC) uses sodium borohydride ($NaBH_4$) or potassium borohydride (KBH_4) in aqueous alkaline solution directly as the fuel. The oxidant used in a DBFC is oxygen, air, or hydrogen peroxide (H_2O_2). Compared with H_2-

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polymer electrolyte fuel cells (H_2-PEFCs), or direct methanol fuel cells (DMFCs), a DBFC has several advantageous thermodynamic characteristics including highest theoretical cell potential and highest number of electron transferred [1]. Other advantages of DBFC systems include:

- DBFCs use liquid fuel which needs no fuel processor.
- Alkaline medium opens up the possibility of using non-noble electrocatalysts and also features low corrosion activity.
- Cooling plates are not necessary in DBFC stacks, since the liquid fuel solution can serve as heat exchange medium to cool the stacks.
- Cathode gas humidifier can be eliminated, since water can be electro-osmotically dragged to the cathode.
- Both borohydride and its oxidation product metaborate are relatively inert and non-toxic. Besides, metaborate can be recycled to produce borohydride.
- With H_2O_2 as an oxidant, DBFC is a suitable power supply for air deficient applications, such as power in submarine or power in space.

When oxygen is employed as the oxidant in the cathode, the net cell reaction is expressed by Eq. (1).

$$BH_4^- + 2O_2 \rightarrow BO_2^- + 2H_2O \quad E^o_{cell} = 1.64\ V \tag{1}$$

The overall cell reaction for DBFC using H_2O_2 as oxidant is expressed by Eq. (2).

$$BH_4^- + 4H_2O_2 \rightarrow BO_2^- + 6H_2O \quad E^o_{cell} = 3.01\ V \tag{2}$$

2. MEA Production

Among the components of a fuel cell, the production of an MEA is the most complicated process. Typical MEA manufacturing proceeds in multiple steps, such as catalyst ink preparation followed by catalyst coating and drying. This is followed by pressing membrane and electrode together. Fig.1 describes the flowchart for manufacturing process of the MEA for a DBFC. Estimated cost of the first step, which is catalyst ink preparation, is $20 per 100 MEA [2]. For H_2-PEFC or DMFC, hot pressing technique is usually employed to make MEA. Estimated cost of hot-pressing process is $ 130 per 100 MEA [2]. During assembly of a DBFC, membrane is held together between two electrodes by mechanical force. Hot-pressing process, which is used in preparation of MEA of a H_2-PEFC or DMFC, is not needed for DBFC. In fact, it is useful to leave some space between the anode and the membrane so that the fuel being in liquid state would be able to reach the anode easily and also the release of hydrogen evolved by decomposition/hydrolysis of BH_4^- fuel would be facilitated [3]. Cost and power performance are two important factors which affect the commercialization of fuel cells. Membrane-electrode-assembly (MEA) is a key component which accounts for over 50% of a fuel cell stack cost [4]. Thus, the development of high performance and cost-effective materials for producing MEA would help in promoting the commercialization of fuel cells. Factors such as high utilization of catalysts, low cost mass manufacturing process, etc. can also contribute to the cost reduction. This paper discusses some of the recent advances made in achieving high power performance with cost-effective MEA materials in a DBFC.

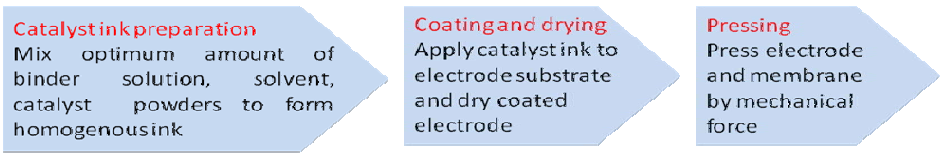

Fig. 1. Flowchart for preparing an MEA.

3. Electrode Materials

In H_2-PEFCs and DMFCs, Pt is by far the most effective element used as electro-catalysts, and nearly all current polymer electrolyte fuel cells use platinum particles on porous carbon supports to catalyze both hydrogen/methanol oxidation and oxygen reduction. However, due to their high cost, current Pt/C catalysts are too expensive and hinders in its commercialization. A DBFC is operated in alkaline medium, which features faster kinetics and higher chemical stability, as compared to acidic medium. Therefore, a wider range of materials including non-platinum metals are usable for both anode and cathode. A class of "(non-precious metal)/(heteroatomic polymer)" catalyst, particularly cobalt-polypyrrole-carbon (Co-PPY-C) has been synthesized by a chemical method and employed as cathode catalyst for oxygen reduction reaction in a DBFC. The DBFC based on Co-PPY-C cathode achieved a peak power density comparable to that of Pt/C [5].

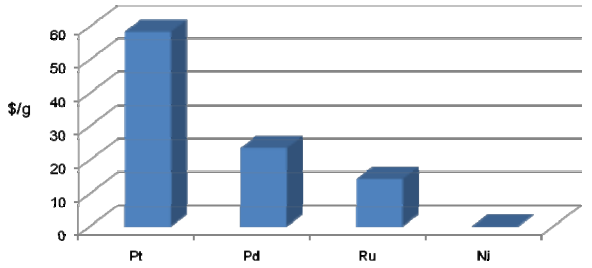

Fig.2. Price comparison of different metals used as catalyst materials for fuel cells (as of Sept 2011).

Borohydride ions readily undergo electro-oxidation on non-precious metallic materials, such as Ni and hydrogen storage alloys. As shown in Fig.2, the price of metal Ni is significantly lower than that of Pt and other metals commonly employed as electrode catalysts for a fuel cell. Thus, the use of Ni catalyst can reduce material cost of an electrode. Ni-based composite has been developed as anode catalyst and has shown both high catalytic activity and fuel efficiency for borohydride oxidation reaction [6,7]. A borohydride-hydrogen peroxide fuel cell was assembled and tested with Ni-based composite anode prepared by ink paste method and Pd cathode prepared by electrodeposition. As shown in Fig.3, peak power densities of 344 mW cm^{-2} and 671 mW cm^{-2} have been achieved at 28 ^oC and 60 ^oC, respectively. Table 1 summarizes some important features of this DBFC. Thus, a high power performance of a DBFC can be achieved with cost-effective electrode catalyst materials.

Table 1. Features of a borohydride-H_2O_2 fuel cell using Ni-based composite anode.

Cell component	Units	Current system
Temperature	^oC	60
Peak power density	mW/cm^2	671
Open circuit potential	V	1.7
Active area	cm^2	5
Membrane type		Nafion
Membrane thickness	micron meter	50
Catalyst loading	mg/cm^2	5
Electrode binder		Nafion
Binder loading	% of catalyst	10
Electrode substrate		Toray carbon paper
Electrode substrate thickness	mil	10

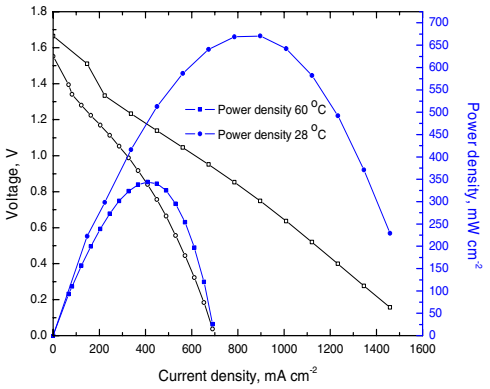

Fig.3. Cell polarization and power density plots for borohydride-H_2O_2 fuel cell using Ni-based composite anode.

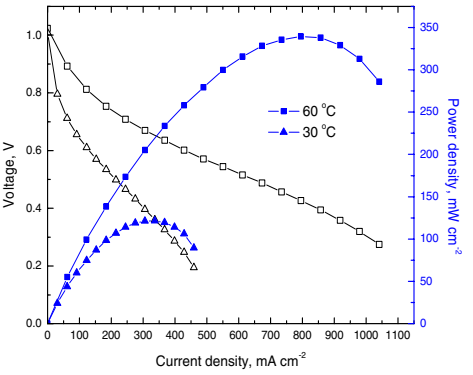

Fig.4. Cell polarization and power density plots for borohydride-oxygen fuel cell using Ni+Pt anode prepared by PVD.

A lot of research has been devoted to reducing the amount of catalysts used in the electrode. Thin layer coating on electrode substrate with cost effective large volume manufacturing protocols employing intelligent process controls would provide increased yield and product uniformity. Physical vapor deposition (PVD) methods afford advantages over traditional means of catalyst coating. These include production of a thin layer of nano-sized particles with high electrochemical surface area, dramatic reduction in materials required, and the ability to reproducibly form controlled film composition and morphology with minimal impurity incorporation. PVD is the excellent method for mass production of small sized electrodes at low cost for micro fuel cell applications. An electrode was prepared by depositing a thickness of 200 angstroms of Ni, followed by a thickness of 10 angstroms of Pt on Ni foam electrode substrate by the authors. This electrode has been employed as anode and tested in a borohydride -oxygen fuel cell. As shown in Fig.4, peak power densities of 121 mW cm^{-2} and 339 mW cm^{-2} have been achieved at 30 ^oC and 60 ^oC, respectively.

4. Membrane and Electrode Binder Materials

Perfluorosulfonic acid (Nafion®) is widely employed as membrane electrolyte and electrode binder materials in fuel cells. However, Nafion® used as binder and for making membrane is expensive and it loses its ionic conductivity if not sufficiently hydrated. Thus, its replacement by cost-effective polymer materials is highly desirable. High performance and cost-effective polymer material has been developed as membrane and electrode binder for DBFCs. This polymeric material is a chemical hydrogel based on either polyvinyl alcohol (PVA) or chitosan. PVA is a cheap, non-toxic, and chemically stable synthetic polymer used in a wide range of industrial, commercial, medical, and food applications [8]. Under acidic conditions, the –OH groups of PVA react with –CHO groups of certain aldehydes to form acetal or hemiacetal linkages [9], and the resultant polymeric entity can be termed as PVA chemical hydrogel. Chitosan is an inexpensive, biodegradable, and non-toxic natural polymer that is derived by deacetylation of chitin. Chitin, which is present in the exoskeleton of arthropods, is the second most abundant natural biopolymer next to cellulose [10]. Chitosan is soluble in dilute aqueous solution of a weak organic acid. Dissolved chitosan reacts with dialdehydes, particularly with glutaraldehyde, to form covalent imine

bonds, and the resultant polymeric entity is termed as chitosan chemical hydrogel. Chitosan, being a polycation, can also be crosslinked ionically with sulfate, phosphate, etc. Both PVA and chitosan chemical hydrogel have been employed as electrode binder for a DBFC using hydrogen peroxide as oxidant, and their power performance has been compared with a Nafion® binder-based DBFC [11]. Both fuel cells used cost-effective hydrogen storage alloys as catalysts. PVA chemical hydrogel binder demonstrated power performance as good as a DBFC employing Nafion® binder. Chitosan chemical hydrogel gave superior performance compared to Nafion® binder. It should be noted that with PVA or chitosan chemical hydrogel, a much smaller amount of binder is needed for the same amount of catalysts as compared with Nafion® binder. Catalyst ink with polymeric binders such as Nafion® is generally prepared with organic solvent, particularly 2-propanol, because of the high hydrophobic nature of long carbon chain of polymers. Use of organic solvents not only adds to the cost of MEA but also cause health and environmental hazards. Catalyst ink with PVA and chitosan chemical hydrogel binders is prepared in water, thereby enhancing cost-effective and environmentally benign electrode production technologies. In addition to binder materials, PVA and chitosan can also be used to prepare membrane electrolyte for use in a fuel cell. Crosslinked PVA and crosslinked chitosan membrane have been prepared by a solution casting method by the authors [12,13]. PVA hydrogel membrane achieved comparable power performance as Nafion® membrane in a borohydride-oxygen fuel cell [12]. Crosslinked chitosan membrane demonstrated superior power performance to the Nafion® membrane [13, 14]. At an elevated temperature, a DBFC employing crosslinked chitosan membrane and chitosan chemical hydrogel binder gave as good short-term stability for 100 hours as a Nafion®-based DBFC [14]. Recent laboratory tests using chitosan membrane, chitosan chemical hydrogel binder, and Ni-based composite anode in a borohydride-oxygen fuel cell have resulted in a peak power density of 800 mW cm^{-2} at 70 ^{o}C (Fig.5). Table 2 describes features of this DBFC. Fig.6 shows a picture of a chitosan membrane prepared by a tape casting method. This low-cost membrane made from a natural biopolymer chitosan is developed and used in a DBFC for the first time by the authors. Preliminary cost estimates for chitosan membranes range from \$20-30/m^2, which is more than an order of magnitude lower than the current cost of Nafion® membranes, which range from \$500-1000/m^2 depending on the type and quantity ordered [15]. Thus, chitosan membrane is able to perform significantly better than the commercial perfluorosulfonated membranes, such as Nafion® and costs less than 10% of Nafion®.

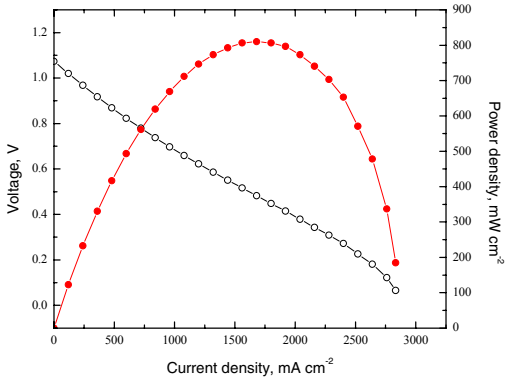

Fig.5. Cell polarization and power density plots for a borohydride-oxygen fuel cell using crosslinked chitosan membrane, chitosan binder, and Ni-based composite anode.

Fig.6. A picture of a crosslinked chitosan membrane folded in half.

Table 2. Features of a borohydride-oxygen fuel cell.

Cell component	Units	Current system
Temperature	^{o}C	70
Peak power density	mW/cm^2	800
Open circuit potential	V	1.07
Active area	cm^2	5
Membrane type		Chitosan
Membrane thickness	micron meter	~45
Catalyst loading	mg/cm^2	5
Catalyst binder		Chitosan
Binder loading	% of catalyst	2
Electrode substrate		Ni foam
electrode substrate thickness	mm	0.5

5. Conclusions

Direct borohydride fuel cell is a promising fuel cell, especially for portable applications. The use of hydrogen peroxide as an oxidant is good for air deficient applications, such as for power in submarine or power in space. Various studies have demonstrated that a DBFC is able to give high power performance with low-cost MEA materials. The use of Ni-based anode, chitosan membrane and binder would reduce cost of DBFC and thus would help in its commercialization. Cost of various production steps and that of polymer membrane electrolyte are presented.

Acknowledgements

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